

Best Available Copy

REFERENCE

PATENT SPECIFICATION

NO DRAWINGS

1,121,567



Date of Application and filing Complete Specification: 20 September, 1966.

1,121,567

No. 41993/66

Application made in United States of America (No. 489416) on 22 September, 1965.

Complete Specification Published: 31 July, 1968

© Crown Copyright, 1968.

Index at Acceptance:—C5 F (452, 462, 474, 475, 476, 482, 548, 595, 623, 633, 649, 673, 695, 743, 792, A).

Int. Cl.:—C 10 m 1/46.

COMPLETE SPECIFICATION

Preservation of Elastomeric Members

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, the Netherlands, do hereby declare he invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the preservation of an elastomeric member, for example an elastomeric seal. More particularly, it concerns a method of combating damage of an elastomeric member by a lubricating oil, and a composition suitable for use as a hydraulic fluid or as a lubricant.

According to one aspect of the present invention, a method of combating damage of an elastomeric member by a lubricating oil comprises bringing into contact with the elastomeric member the lubricating oil (which may be a mineral lubricating oil and/or a synthetic lubricating oil) together with a minor amount of an aryl di-[(C₁₋₃)_n alkaryl] phosphate and/or a diaryl (C₁₋₃)_n alkaryl phosphate, wherein *n* is 1 to 4.

The method enables damage of the elastomeric member by the lubricating oil to be reduced or perhaps even prevented.

30 Thus, for example, resilience of the elastomeric member can be preserved. The elastomeric member can be an elastomer prepared by polymerizing an open chain conjugated diene (for example buta-1,3-diene; isoprene; pentadiene; or chloroprene), or by copolymerizing such a substance with another kind of polymerizable compound (for example acrylonitrile; acrolein; methyl methacrylate; styrene; methyl styrene; a vinyl halide; or a vinyl ester). Important classes of synthetic elastomers are Buna N rubbers (which are copolymers of a buta-1,3-diene and acrylonitrile); Buna

S rubbers (which are copolymers of buta-1,3-diene and styrene); butyl rubbers (which are copolymers of buta-1,3-diene and isobutylene); chloroprene rubbers; and silicone rubbers. As an alternative to being a synthetic elastomer, the elastomeric member can be of a natural rubber.

According to another aspect of the present invention, a composition suitable for use as a hydraulic fluid or as a lubricant (for example as a gear oil) comprises a mineral lubricating oil which is a blended oil comprising 60 to 80% by weight of a mineral lubricating oil having a viscosity index of 85 to 140 and 40 to 20% by weight of a mineral lubricating oil having a viscosity index of 20 to 40, and a minor amount of an aryl di-[(C₁₋₃)_n alkaryl] phosphate and/or a diaryl (C₁₋₃)_n alkaryl phosphate, wherein *n* is 1 to 4. Such a composition is preferred for carrying out the method of the present invention.

A more preferred instance of the blended oil is a blend of 60% by weight of oil A described below and 40% by weight of oil B described below. This blend is called blend A in Compositions I to X given below. Oils A and B have the following properties:

Properties	Oil A	Oil B
Gravity, °API	30.6	25.1
Viscosity, S.S.U. at 100°F	120.7	64.8
Viscosity, S.S.U. at 210°F	41.0	34.9
Viscosity Index	98	35
Specific Dispersion	111	135
Flash Point, °F	390	290
Pour Point, °F	+5	-25
Sulphur, %w	0.13	1.24
Nitrogen, ppm	27	

In practising the method of the present invention or in using the composition of the present invention, the blended lubricating oil may comprise 1 to 15% by weight based

	Composition	Lubrication Oil	Additives
	I	Blend A (see above)	1% by weight diphenyl tolyl phosphate
5	II	Blend A	3% by weight diphenyl tolyl phosphate
	III	Blend A	1% by weight phenyl ditolyl phosphate
	IV	Blend A	1% by weight diphenyl tolyl phosphate + 5% by weight basic Ca petroleum sulphonate (180% basic) + 3% by weight sulphurized sperm oil (9.5% S)
10	V	Blend A	3% by weight diphenyl tolyl phosphate + 5% by weight basic Ca petroleum sulphonate (180% basic) + 3% by weight sulphurized sperm oil (9.5% S) + 1% by weight poly C8-18 alkyl methacrylate ester (MW 10,000-15,000) + 10 ppm dimethyl silicone polymer
15	VI	Blend A	1% by weight diphenyl tolyl phosphate + 5% by weight basic Ca petroleum sulphonate (180% basic) + 3% by weight sulphurized sperm oil (9.5% S) + 5 ppm dimethyl silicone polymer
20	VII	Blend B (70% by weight mineral lubricating oil 90 viscosity index + 30% by weight mineral lubricating oil 35 viscosity index)	1% by weight diphenyl tolyl phosphate + 5% by weight basic Ca petroleum sulphonate (80%) + 5% by weight sulphurized sperm oil (9.5% S)
25	VIII	Blend C (80% by weight mineral lubricating oil 95 viscosity index + 20% by weight mineral lubricating oil 30 viscosity index)	1% by weight diphenyl tolyl phosphate + 5% by weight basic Ca petroleum sulphonate (180% basic) + 3% by weight sulphurized sperm oil (9.5% S) + 5 ppm dimethyl silicone polymer
30	IX	Blend C	1% by weight phenyl ditolyl phosphate + 5% by weight basic Ca petroleum sulphonate (180% basic) + 3% by weight sulphurized sperm oil (9.5% S)
35	X	Blend A	1% by weight diphenyl tolyl phosphate + 2% by weight phenyl ditolyl phos- phate + 5% by weight basic Ca pet- roleum sulphonate (180% basic) + 3% by weight sulphurized sperm oil (9.5% S) + 1% by weight poly C ₈₋₁₈ alkyl metha- crylate ester (MW=10,000-15,000) + 10 ppm dimethyl silicone polymer
40			
45			

The compositions given in the Table below were subjected to the following tests and the results are shown in Table 1.

(X₁) International Harvester Corrosion-Oxidation Test — (100 hours 1.5l/hr. air blown at 275°F with copper, brass, aluminium and iron immersed in test oil).

(X₂) International Harvester High Tem-

perature Rubber Bend Test — (480 hours at 300°F after which rubber in test oil is removed and bent over a mandrel; no cracking or checking allowed).

(X₃) IAE gear machine — Boner-Gear 60 and Transmission Lubricants, pages 235-236.

	Composition	Tests		
		(X ₁)	(X ₂)	(X ₃)
65	IV to VII	Pass	Pass	85-100 lbs.
	1*	Failed	Failed	50 lbs.
	2**	Failed	Failed	Failed, less 30 lbs.
	3***	Failed	Failed	Failed, less 30 lbs.
	Blend (A) neat	Failed	Failed	Failed, less 20 lbs.

1* =same as Composition VI except that 3% by weight tritolyl phosphate used in place of 3% by weight diphenyl tolyl phosphate.

5 2** =same as Composition VI except that 3% by weight triphenyl phosphate used in place of 3% by weight diphenyl tolyl phosphate.

10 3*** =same as Composition VI except that 3% by weight dimethyl phenyl phosphate used in place of diphenyl tolyl phosphate.

Also, substituting for diphenyl tolyl phosphate or phenyl ditolyl phosphate in compositions I, II and III zinc dialkyl dithiophosphate resulted in failures when such compositions were tested in Test X.

WHAT WE CLAIM IS:—

1. A method of combating damage of
20 an elastomeric member by a lubricating oil comprising bringing into contact with the elastomeric member the lubricating oil together with a minor amount of an aryl di-
25 $[(C_{1-3})_n \text{ alkaryl}]$ phosphate and/or a diaryl $(C_{1-3})_n$ alkaryl phosphate, wherein n is 1 to 4.

2. A method as claimed in Claim 1 in which the lubricating oil is a mineral lubricating oil.

30 3. A method as claimed in Claim 2 in which the mineral lubricating oil is a blended oil comprising 60 to 80% by weight of a mineral lubricating oil having a viscosity index of 85 to 140 and 40 to 20%
35 by weight of a mineral lubricating oil having a viscosity index of 20 to 40.

4. A method as claimed in Claim 3 in which, together with the blended oil, there is 1 to 15% by weight based on the weight
40 of the blended oil of a basic polyvalent metal petroleum sulphonate, the acid part of which has a molecular weight of 400 to 1,000.

5. A method as claimed in Claim 4 in which the petroleum sulphonate is 180 to 800% basic.

6. A method as claimed in Claim 4 or Claim 5 in which the petroleum sulphonate is of a metal of Group II of the Periodic
50 Table.

7. A method as claimed in Claim 6 in which the petroleum sulphonate is of an alkaline earth metal.

8. A method as claimed in Claim 7 in which the petroleum sulphonate is of calcium.

9. A method as claimed in Claim 8 in which the petroleum sulphonate is a 180% basic calcium petroleum sulphonate.

60 10. A method as claimed in Claim 8 in which the petroleum sulphonate is a 800% basic calcium petroleum sulphonate.

11. A method as claimed in any of Claims 4 to 10 in which the acid part of
65 the petroleum sulphonate has a molecular

weight of 420 to 600.

12. A method as claimed in any of Claims 3 to 11 in which, together with the blended oil, there is 1 to 15% by weight of a sulphurized fatty oil.

13. A method as claimed in Claim 12 in which the sulphurized fatty oil is a sulphurized sperm oil.

14. A method as claimed in Claim 13 in which the sulphurized sperm oil has 9
75 to 20% by weight of sulphur.

15. A method as claimed in any of Claims 1 to 14 in which there is 1 to 5% by weight, based on the weight of the lubricating oil, of the aryl di- $[(C_{1-3})_n \text{ alkaryl}]$
80 phosphate and/or the diaryl $(C_{1-3})_n$ alkaryl phosphate, wherein n is 1 to 4.

16. A method as claimed in any of Claims 1 to 15 in which a phenyl di- $[(C_{1-3})_n \text{ alkphenyl}]$ phosphate, wherein n is 1 to 4
85 is brought into contact with the elastomeric member.

17. A method as claimed in Claim 16 in which the phenyl di- $[(C_{1-3})_n \text{ alkphenyl}]$ phosphate is phenyl ditolyl phosphate.

18. A method as claimed in any of Claims 1 to 17 in which a diphenyl $(C_{1-3})_n$ alkphenyl phosphate, wherein n is 1 to 4,
95 is brought into contact with the elastomeric member.

19. A method as claimed in Claim 18 in which the diphenyl $(C_{1-3})_n$ alkphenyl phosphate is diphenyl tolyl phosphate.

20. A method as claimed in Claim 1 of combating damage of an elastomeric
100 member by a lubricating oil, substantially as described.

21. A composition suitable for use as a hydraulic fluid or as a lubricant, comprising a mineral lubricating oil which is a blended
105 oil comprising 60 to 80% by weight of a mineral lubricating oil having a viscosity index of 85 to 140 and 40 to 20% by weight of a mineral lubricating oil having a viscosity index of 20 to 40, and a minor
110 amount of an aryl di $[(C_{1-3})_n \text{ alkaryl}]$ phosphate and/or a diaryl $(C_{1-3})_n$ alkaryl phosphate, wherein n is 1 to 4.

22. A composition as claimed in Claim 21 comprising 1 to 15% by weight based on
115 the weight of the blended oil of a basic polyvalent metal petroleum sulphonate, the acid part of which has a molecular weight of 400 to 1,000.

23. A composition as claimed in Claim 22 in which the petroleum sulphonate is 180 to 800% basic.

24. A composition as claimed in Claim 22 or Claim 23 in which the petroleum sulphonate is of a metal of Group II of
125 the Periodic Table.

25. A composition as claimed in Claim 24 in which the petroleum sulphonate is of an alkaline earth metal.

26. A composition as claimed in Claim 130

25 in which the petroleum sulphonate is of calcium.

27. A composition as claimed in Claim

26 in which the petroleum sulphonate is a 5 180% basic calcium petroleum sulphonate.

28. A composition as claimed in Claim 26 in which the petroleum sulphonate is a 800% basic calcium petroleum sulphonate.

29. A composition as claimed in any of 10 Claims 22 to 28 in which the acid part of the petroleum sulphonate has a molecular weight of 420 to 600.

30. A composition as claimed in any of Claims 21 to 29 comprising 1 to 15% by 15 weight of a sulphurized fatty oil.

31. A composition as claimed in Claim 30 in which the sulphurized fatty oil is a sulphurized sperm oil.

32. A composition as claimed in Claim 20 31 in which the sulphurized sperm oil has 9 to 20% by weight of sulphur.

33. A composition as claimed in any of Claims 21 to 32 in which there is 1 to 5% by weight based on the lubricating oil, of

the aryl di- $[(C_{1-8})_n \text{ alkaryl}]$ phosphate and/ 25 or the diaryl $(C_{1-8})_n$ alkaryl phosphate, wherein n is 1 to 4.

34. A composition as claimed in any of Claims 21 to 33 in which there is a phenyl di- $[(C_{1-8})_n \text{ alkphenyl}]$ phosphate, wherein n 30 is 1 to 4.

35. A composition as claimed in Claim 34 in which the phenyl di- $[(C_{1-8})_n \text{ alkphenyl}]$ phosphate is phenyl ditolyl phosphate.

36. A composition as claimed in any of 35 Claims 21 to 35 in which there is a diphenyl $(C_{1-8})_n$ alkphenyl phosphate, wherein n is 1 to 4.

37. A composition as claimed in Claim 36 in which the diphenyl $(C_{1-8})_n$ alkphenyl 40 phosphate is diphenyl tolyl phosphate.

38. Compositions I to X as described.

39. A composition as claimed in Claim 21 and substantially as described.

KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.